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(54) IMPROVED HYDROGENATION OF CONJUGATED DIENE POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To stably attain high hydrogenation rate in a shortened time in an industrial scale with a reduced amount of the catalyst as much as possible, when a conjugated diene polymer is hydrogenated by using a metallocene hydrogenation catalyst in a large reactor vessel.

SOLUTION: When a conjugated diene polymer produced by using an organometallic compound of alkali (for example, n-propyllithium) as a polymerization initiator is hydrogenated over a metallocene hydrogenation catalyst, the catalyst is added in two or more portions to obtain the conjugated diene polymer of $\geq 98\%$ hydrogenation rate. In a preferred embodiment, a reactor vessel of ≥ 10 m³ capacity is used, and the catalyst is added in 2-5 portions including the first addition where the catalyst is added at least once when the hydrogenation rate reaches 60-95%. The conjugated diene for this diene polymer is preferably 1,3-butadiene or isoprene.

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CLAIMS

[Claim(s)]

[Claim 1] The hydrogenation technique of the improved conjugated-diene system polymer which is characterized by adding catalysts for hydrogenation in 2 steps or more, and advancing hydrogenation in case the conjugated-diene system polymer which made the organoalkali metal compound the polymerization initiator and carried out the polymerization is hydrogenated using metallocene system catalysts for hydrogenation and the conjugated-diene system polymer of 98% or more of the rates of hydrogenation is obtained.

[Claim 2] The hydrogenation technique of the improved conjugated-diene system polymer which is characterized by using catalysts for hydrogenation once or more in a claim 1 when the rate of hydrogenation of a conjugated-diene system polymer is 60% - 95%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the technique of contacting in hydrogen the conjugated-diene system polymer which made the organoalkali metal compound the polymerization initiator and carried out the polymerization using metallocene system catalysts for hydrogenation, and hydrogenating the double bond of a conjugated diene. Furthermore, in case the conjugated-diene system polymer of 98% or more of the rate of hydrogenation is industrially obtained using three or more big 1m reaction containers in that case, it is related with the technique of hydrogenating economically stably for a short time, by dividing catalysts for hydrogenation into several order, and adding.

[0002]

[Description of the Prior Art] There is the characteristic feature of finishing the hydrogenation of the amount of said in a few amount under a milder condition if it compares with a nickel system catalyst when using for hydrogenation (it abbreviates to a hydrogenation below) of a polymerization object, a metallocene system catalyst has special unnecessary processing which removes a residual catalyst difference after a hydrogenation for this reason, and since this is the characteristic feature that processing which removes a residual catalyst difference is light, and ends when carrying out even if, it has often come to be used in recent years. However, since price has the problem are easy to lose activity highly and easily, conventionally, a metallocene system catalyst is high activity more, and the hydrogenation catalyst with a sufficient long-term-storage stability with easy how to deal with it was examined variously, and it has been proposed. For example, a specific titanocene compound and a specific alkyl lithium are combined. How to carry out the hydrogenation of the olefin compound (JP,61-33132,A, JP,1-53851,A), the technique (JP,61-28507,A) of combining with a metallocene compound, and organic aluminum, zinc and magnesium, coming out, and carrying out the hydrogenation of the olefin nature unsaturation (**) polymerization object the technique (JP,61-47706,A) of carrying out the hydrogenation of the olefin nature unsaturation machine inclusion living polymer in the combination of No. 209103 [62 to], a specific titanocene compound, and an alkyl lithium JP,63-5402,A, How to carry out the hydrogenation of the olefin nature double bond in the olefin nature unsaturation double bond inclusion polymer by the reactant which combined Tebbe reagent which are a titanocene compound and the ***** cycle compound of a trimethylaluminum, and the alkyl alkali metal compound (U.S. JP,5244980,B), How to combine a titanocene compound with the lithium ***** site of the specified amount, and carry out the hydrogenation of the olefin nature double bond in an olefin nature unsaturation double bond inclusion polymer (JP,1-275605,A), Technique, such as the technique (Japanese Patent Application No. 9-252180) of carrying out the hydrogenation of the conjugated-diene polymerization object by the system in which organoaluminum-compound others were made to exist by specific proportion, is proposed using the metallocene system hydrogenation catalyst.

[0003]

[Problem(s) to be Solved by the Invention] However, also in which such technique, when it was actually going to obtain the conjugated-diene system polymer of 98% or more of the rate of a high hydrogenation within three or more big 1m reaction containers industrially, and hydrogenation conditions were changed by the temperature change etc. or it reduced for economical efficiency pursuit of the amount of the catalyst used, hydrogenation time was taken for a long time, and troubles — the polymer of the target rate of a high hydrogenation is not obtained greatly — arose. For this reason, enhancement of the hydrogenation technique for attaining a high hydrogenation stably industrially for a short time was desired by as few the amount of the catalyst used as possible.

[0004]

[Means for Solving the Problem] As a result of inquiring zealously that the above-mentioned trouble of the conventional technique should be solved, when a hydrogenation is performed within such three or more big 1m reaction containers, dividing a hydrogenation catalyst into several order and adding, and by surely *****ing a catalyst once or more at the specific rate of a hydrogenation desirable especially, this invention persons find out industrially the technique of attaining the hydrogenation of the rate of a high hydrogenation, economically stably for a short time, and came to accomplish this invention.

[0005] Three or more big 10m reaction containers are preferably used for this invention still preferably three or more [5m] three or more [1m]. industrially The hydrogenation of the conjugated-diene system polymer which made the organoalkali metal compound the polymerization initiator and carried out the polymerization is carried out using a metallocene system hydrogenation catalyst. adding a hydrogenation catalyst in 2 - 10 steps preferably twice or more, and advancing a hydrogenation, in case the conjugated-diene system polymer of 98% or more of the rates of a hydrogenation is obtained — still preferably When the rate of a hydrogenation of a polymer is 60% - 95%, it is the hydrogenation technique of the improved conjugated-diene system polymer which is characterized by *****ing a hydrogenation catalyst once or more.

[0006] The aliphatic hydrocarbon alkali metal compound by which it is known that there is generally anionic polymerization activity to a conjugated-diene compound, an aromatic-hydrocarbon alkali metal compound, an organic amino alkali metal compound, etc. are contained, and the organoalkali metal compounds used as a polymerization initiator by this invention are a lithium, sodium, a potassium, etc. as alkali metal. The compound which is the aliphatic series and the aromatic-hydrocarbon lithium compound of carbon numbers 1-20, and contains one lithium in 1 molecule as a suitable organoalkali metal compound, the dilithium compound which contains two or more lithiums in 1 molecule, a ***** compound, and a tetrapod lithium compound are contained. Specifically, the resultant of

the resultant of n-propyl lithium, n-butyl lithium, sec-butyl lithium, tert-butyl lithium, isopentyl lithium, n-hexyl lithium, n-octyl lithium, a phenyl lithium, a tolyl lithium, and diisopropenylbenzene and sec-butyl lithium, 1 [little], and 3-butadiene etc. is further raised with a divinylbenzene and sec-butyl lithium.

[0007] The conjugated-diene system polymer of this invention contains 1 which has of fin double combination which is the gay polymer of a conjugated diene, the copolymer of a conjugated diene which consists of two or more sorts of conjugated dienes, and the copolymer of a conjugated diene and other monomers which can be copolymerized, and originates from a conjugated diene in this polymer, 4-polymer, 1, 2 or 3, and 4-polymer. As a conjugated diene, 1, 3-butadiene, an isoprene, 2, the 3-dimethyl-1, 3-butadiene, 1, 3-pentadiene, the 2-methyl-1, 3-pentadiene, 1, 3-hexadiene, 4, the 5-diethyl-1, 3-***** diene, 3-butyl-1, 3-***** diene, etc. are mentioned to the conjugated diene and concrete target which have the carbon atom of carbon numbers 4-20. 1 [****] / when obtaining the elastic body which could develop advantageously industrially and was excellent in physical properties, 3-butadiene, and an isoprene are desirable. Moreover, a thing typical as a conjugated diene and other monomers which can be copolymerized is a vinyl aromatic compound. For example, styrene, alpha-methyl-styrene, p-methyl-styrene, divinylbenzene, 1, and 1-diphenylethylene, N, and N-dimethyl-p-aminoethyl styrene, N, and N-diethyl-p-aminoethyl styrene etc. is raised, and they are styrene and an alpha methyl styrene preferably. These copolymers are randomness or a block copolymer.

[0008] Although a hydrogenation is usually performed in an inert hydrocarbon solvent, as this inert hydrocarbon solvent, it is the solvent of a conjugated-diene system polymer, and does not have a bad influence on a reaction in the case of hydrogenation. It is desirable that continue further at a polymerization and hydrogenation is performed in the same inert hydrocarbon solvent at this invention. The aromatic hydrocarbon like the alicyclic hydrocarbon like for example, n-butane, an isobutane, n-pentane, n-hexane, n-heptane, the aliphatic hydrocarbon like n-octane, a cyclohexane, cycloheptane, and methyl cycloheptane and benzene, toluene, a xylene, and ethylbenzene can also use a suitable solvent under the selected hydrogenation condition only within the time of the hydrogenation of the aromatic double bond not being carried out. Concentration of the conjugated-diene system polymer melted in this solvent is preferably made into 10 - 30% of concentration five to 40%. It is not desirable in order for the load of the back process which will separate a conjugated-diene system polymer and a solvent if this concentration is lower than 5% to become large, for viscosity to become high greatly preferably if it is the concentration exceeding 40%, and for miscibilities and heat-conducting characteristic, such as hydrogen and a hydrogenation catalyst, to fall, as a result to influence a hydrogenation reaction.

[0009] As a ligand, the metallocene system hydrogenation catalysts used by this invention are organometallic compounds, such as titanium with an identity or two different cyclopentadienyl groups (substitute), a zirconium, and a hafnium, and are used with a desirable reducing organometallic compound, for example, an alkyl lithium, alkyl magnesium, alkylaluminum, a dialkylzinc, etc. Every technique is employable if it is the hydrogenation technique using a metallocene system compound as the hydrogenation technique. For example, a specific titanocene compound and a specific alkyl lithium are combined. How to carry out the hydrogenation of the olefin compound (JP,61-33132,A, JP,1-53851,A), the technique (JP,61-28507,A) of combining with a metallocene compound, and organic aluminum, zinc and magnesium, coming out, and carrying out the hydrogenation of the olefin nature unsaturation (**), polymerization object the technique (JP,61-47706,A) of carrying out the hydrogenation of the olefin nature unsaturation machine inclusion living polymer in the combination of No. 209103 [62 to], a specific titanocene compound, and an alkyl lithium JP,63-5402,A, How to carry out the hydrogenation of the olefin nature double bond in the olefin nature unsaturation double bond inclusion polymer by the reactant which combined Tebbe reagent which are a titanocene compound and the ***** cycle compound of a trimethylaluminum, and the alkyl alkali metal compound (U.S. JP,5244980,B), How to combine a titanocene compound with the lithium ***** site of the specified amount, and carry out the hydrogenation of the olefin nature double bond in an olefin nature unsaturation double bond inclusion polymer (JP,1-275605,A), The technique of any **, such as the technique (Japanese Patent Application No. 9-252180) of carrying out the hydrogenation of the conjugated-diene polymerization object using a metallocene system hydrogenation catalyst by the system in which organoaluminum-compound others were made to exist by specific proportion, may be used. Moreover, the technique which also doubled hydrogenation conditions with such a hydrogenation catalyst and which was written to each specification can be used.

[0010] Such a hydrogenation catalyst is preferably divided into 2 - 10 times twice or more including 1 time of the beginning, and it adds in 2 - 5 steps still preferably. In this case, it divides into a minimum of 2 times, and preferably, when the rate of a hydrogenation of a polymer is 60% - 95%, it is very important to **** a hydrogenation catalyst once [at least] or more still preferably at 70% - 95% of the time. That is, if a hydrogenation is performed within three or more industrial 1m reaction containers using a metallocene system hydrogenation catalyst and the rate of a hydrogenation of a polymer polymer solution will rise with 60% - 95%, viscosity will also rise sharply, cooling capacity will get worse, and it will become easy to generate a local temperature rise. Especially a hydrogenation reaction is intense exothermic reaction, and this inclination is remarkable. If a local temperature rise occurs, it will activate increasingly, and the hydrogenation reaction of the fraction will cause the further generation of heat, and will trigger the deactivation reaction of the catalyst which the activity of a hydrogenation catalyst finally loses. For this reason, a fall of a hydrogenation reaction and troubles -- the polymer of the target rate of a high hydrogenation is not obtained greatly -- tend to arise as a result. This phenomenon of the more large-sized reactor is more remarkable, and is a big technical problem at the time of performing a industrial production. However, when such a rate of a hydrogenation is reached, by ****ing a catalyst, when required, the activity catalyst of a complement can be supplied, and it is enabled to carry out a hydrogenation until it obtains the polymer of a rate of a high hydrogenation called 98% or more certainly [in a short time] and stably rather at least as all amount of the catalyst used by ****ing to multi-stage. Although it may activate it after the amount of [first] 1st addition touches a hydrogenation catalyst with a polymer, as for a **** catalyst, it is desirable to add in the status to activate immediately in the hydrogen ambient atmosphere after discovering hydrogenation activity at least. Although the catalyst of a part for first time addition and post-addition may not be the same object, the same object of the hydrogenation catalyst of several addition is more desirable from the simple nature of operation. Furthermore, operation becomes complicated, and 2 to 10 times, it is not desirable and is [adding in 11 steps or more] is compatible in operability, and catalyst luminous efficacy and hydrogenation certainty, and [desirably desirable [a thing / putting in in 2 - 3 steps still desirably] 2 to 5 times. As the technique of distinguishing 70% - 95% of a time still preferably, you may distinguish on the basis of the index of what **, such as measurement of the amount of survival of the double bond of a conjugated-diene system polymer by which the

hydrogenation was carried out, calculated from the used amount of hydrogen gas, the hydrogen pressure force change in a hydrogenation container, and hydrogenation time, the time of the rate of a hydrogenation of a polymer which is the catalyst stage being 60% - 95%. Furthermore, the time of the rate of a hydrogenation of a polymer being 60% - 95% - further - desirable - 70% - 95% of a time - the inside of a specific container - a batch type or a continuity - and - or a hydrogenation is performed to a batch process, a hydrogenation catalyst is added and the hydrogenation of the remaining fraction may be performed to 98% within another container or piping. Anyway, by dividing in this way and adding a hydrogenation catalyst, it is efficient, and moreover, it is stable and a hydrogenation can be performed industrially certainly. In addition, the rate of a hydrogenation in this invention means the rate of a hydrogenation of the conjugated-diene unit included in a polymer.

[0011]

[Example] Although the following examples explain this invention concretely, this invention is not limited to these. The synthetic example of each living polymer (A polymer and B polymer) used for the example was shown in the following examples of a manufacture.

[0012] After putting in 4.3t of cyclohexanes, and 0.20t of styrene monomers into the reactor with an agitator of 3 116m of the examples of a manufacture, 4.8kg of 15% n-butyl-lithium solutions, tetramethylethylenediamine 0.62kg was added further, initial temperature was set as 70 degrees C, and the polymerization was carried out for 40 minutes under churning. Subsequently, 3.08t of the cyclohexane solutions which contain 1 and 3 butadiene monomer 30% was added, and they carried out the polymerization for 1 hour. Furthermore, 0.66t of the cyclohexane solutions which contain a styrene monomer 30% was added, and they carried out the polymerization for 40 minutes. The peak temperature at the time of a polymerization was 82 degrees C. The obtained living polymer (A polymer) was a styrene-styrene-butadiene-rubber type living block polymer whose number average molecular weight it is 1 of 30% of combined-styrene contents, 30% of block styrene contents, and a butadiene unit, and 37% of 2-vinyl joint contents, and is about 230,000.

[0013] After putting in 4.85t of cyclohexanes, and 0.33t of styrene monomers into the reactor with an agitator of 3 216m of the examples of a manufacture, 22kg of 15% n-butyl-lithium solutions was added, tetramethylethylenediamine 1.7kg was added further, initial temperature was set as 70 degrees C, and the polymerization was carried out under churning for 30 minutes. Subsequently, 5.18t of the cyclohexane solutions which contain 1 and 3 butadiene monomer 30% was added, and they carried out the polymerization for 45 minutes. Furthermore, 1.11t of the cyclohexane solutions which contain a styrene monomer 30% was added, and they carried out the polymerization for 30 minutes. The peak temperature at the time of a polymerization was 85 degrees C. The number average molecular weight whose obtained living polymers (B polymer) are 1 of 30% of combined-styrene contents, 30% of block styrene contents, and a butadiene unit and 39% of 2-vinyl joint contents was the styrene-styrene-butadiene-rubber type living block polymer of abbreviation 61,000.

[0014] Hydrogenation catalyst manufacture was performed by the technique based on the technique of example 1 JP,8-33846,A. namely, screw (cyclopentadienyl) *****-p-tolyl (TPM) 6kg - cyclohexane 526kg - it melts in inside and liquefied - 15% butyl-lithium solution after adding 1 and 2 polybutadiene 60kg - 7.1kg addition - further, add, and ethanol 0.6kg was made to react and was prepared as a hydrogenation catalyst (TPM/Li). On the other hand, as pretreatment of a hydrogenation, the cyclohexane which carried out refining xeransis was added, it adjusted to the cyclohexane solution of 11% of polymer concentration, and 0.8 equivalent mol part ethyl alcohol of n-butyl lithium which is a polymerization catalyst further was added to the living-polymer (A polymer) solution obtained in the example 1 of a manufacture. The whole-quantity migration of this polymer solution was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Here, 20 ppm (TPM/Li) of the hydrogenation catalysts which prepared the point were added to the polymer weight on Ti weight criteria here, and the hydrogenation was started. The rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 70% 23 minutes after, at this time, further, 20 ppm (TPM/Li) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. It was 99.9%, when the hydrogenation was ended and the rate of a hydrogenation of a polymer was measured by the NMR method, since the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 100% 35 minutes after and the absorption to the polymer solution of hydrogen was also stopped. In addition, the highest attainment temperature in a hydrogenation was 95 degrees C.

[0015] After pretreating the living-polymer (A polymer) solution obtained by the same technique as the example 1 of example of comparison 1 manufacture by the same technique as an example 1, the whole-quantity migration of it was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor and it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. The hydrogenation catalyst (TPM/Li) prepared by the same technique as an example 1 was added so that it might be set to 40 ppm to a polymer weight on Ti weight criteria at this, and the hydrogenation was started. 65 minutes after, although there was a rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas at 97%, since the absorption to the polymer solution of hydrogen had stopped mostly, the hydrogenation was ended. The rate of a hydrogenation of the last polymer by the NMR method was 96.8%. In addition, the highest attainment temperature in a hydrogenation was 100 degrees C.

[0016] After having added the cyclohexane which carried out refining xeransis to the living polymer (B polymer) obtained in the example 2 of a manufacture and adjusting to the cyclohexane solution of 19% of polymer concentration as example 2 pretreatment, ethyl alcohol was added by 0.9 equivalent mol of n-butyl lithium. Subsequently, the whole-quantity migration of this polymer solution was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. The hydrogenation catalyst (TPM/Li) prepared by the same technique as an example 1 was added in the reaction container, and the hydrogenation was started so that it might be set to 10 ppm to a polymer weight on Ti weight criteria. 35 minutes after, the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 61%, the hydrogenation catalyst (TPM/Li) of the amount set to 5 ppm on Ti weight criteria at this time was added, and the hydrogenation was continued. 40 minutes after, when the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas was 85%, 5 ppm was further added on Ti weight criteria, and the hydrogenation was continued. It was 99.8%, when the hydrogenation was ended and the rate of a hydrogenation of a polymer was

measured by the NMR method, since the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 100% 45 minutes after and the absorption to the polymer solution of hydrogen was also stopped. In addition, the highest attainment temperature in a hydrogenation was 90 degrees C.

[0017] After pretreating the living-polymer (B polymer) solution obtained by the same technique as the example 2 of example of comparison 2 manufactured by the same technique as an example 2, the whole-quantity migration of it was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Furthermore, 20 ppm (TPM/Li) of the hydrogenation catalysts prepared by the same technique as an example 1 were added to the polymer weight on Ti weight criteria, and the hydrogenation was started. 105 minutes after, when the hydrogenation was ended and the rate of a hydrogenation of the last polymer by the NMR method was measured since the absorption to the polymer solution of hydrogen had stopped mostly although there was a rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas at 85%, the rate of a hydrogenation was 85.1%. In addition, the highest attainment temperature in a hydrogenation was 95 degrees C.

[0018] Hydrogenation catalyst manufacture was performed by the technique based on the technique of example 3 Japanese Patent Application No. 9-252180. Added screw (cyclopentadienyl) titanium dichloride 5kg to cyclohexan 70.1kg, and added 24.9kg of trimethylaluminum solutions 10%, and it was made to react after churning for 72 hours, and prepared as a hydrogenation catalyst (TC/TMAL) solution. On the other hand, after pretreating the same living-polymer (A polymer) solution by the same technique as an example 1 as having been obtained in the example 1 of a manufacture, the whole-quantity migration was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Here, 30 ppm (TC/TMAL) of the hydrogenation catalysts which prepared the point were added to the polymer weight on Ti weight criteria here, and the hydrogenation was started. The rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 65% 20 minutes after, at this time, 20 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. 23 minutes after, when the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 80%, 10 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. Furthermore, after [of hydrogenation start] 27 minutes, when the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 90%, 10 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. It was 100%, when the hydrogenation was ended and the rate of a hydrogenation of a polymer was measured by the NMR method, since the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 100% 30 minutes after and the absorption to the polymer solution of hydrogen was also stopped. In addition, the highest attainment temperature in a hydrogenation was 98 degrees C.

[0019] After pretreating the living-polymer (A polymer) solution obtained by the same technique as the example 1 of example of comparison 3 manufactured by the same technique as an example 1, the whole-quantity migration of it was carried out 20m at the reactor with an agitator of 3. After setting the inside of a reactor as 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Furthermore, 70 ppm (TC/TMAL) of the hydrogenation catalysts prepared by the same technique as an example 3 were added to the polymer weight on Ti weight criteria, and the hydrogenation was started. There was a rate of a hydrogenation of the polymer seen from the consumption of the hydrogen gas of 30 minutes after at 91%, the absorption to the polymer solution of hydrogen was also stopped mostly, and the rate of a hydrogenation of the polymer by the NMR method was 91.0%. In addition, the highest attainment temperature in a hydrogenation was 102 degrees C.

[0020] After pretreating the living-polymer (B polymer) solution obtained by the same technique as the example 2 of example 4 manufactured by the same technique as an example 2, the whole-quantity migration of it was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Furthermore, 15 ppm (TC/TMAL) of the hydrogenation catalysts prepared by the same technique as an example 3 were added to the polymer weight on Ti weight criteria, and the hydrogenation was started. The rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 75% 25 minutes after, at this time, 5 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. 29 minutes after, when the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas was 88%, 5 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. Furthermore, after [of hydrogenation start] 32 minutes, when the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas was 93%, 5 more ppm (TC/TMAL) of hydrogenation catalysts were added on Ti weight criteria, and the hydrogenation was continued. It was 99.9%, when the hydrogenation was ended and the rate of a hydrogenation of a polymer was measured by the NMR method, since the rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas became 100% 35 minutes after and the absorption to the polymer solution of hydrogen was also stopped. In addition, the highest attainment temperature in a hydrogenation was 89 degrees C.

[0021] After pretreating the living-polymer (B polymer) solution obtained by the same technique as the example 2 of example of comparison 4 manufactured by the same technique as an example 2, the whole-quantity migration of it was carried out 20m at the reactor with an agitator of 3. After setting up the inside of a reactor in initial temperature of 80 degrees C under churning, hydrogen gas replaced the inside of a reactor, and also it considered as the bottom of the hydrogen gas pressurization of 0.7MPa. Furthermore, 30 ppm (TC/TMAL) of the hydrogenation catalysts prepared by the same technique as an example 3 were added to the polymer weight on Ti weight criteria, and the hydrogenation was started. 70 minutes after, there is a rate of a hydrogenation of the polymer seen from the consumption of hydrogen gas at 89%, and the absorption to the polymer solution of hydrogen also stopped it mostly. The rate of a hydrogenation of the polymer by the NMR method in this time was 89.2%. In addition, the highest attainment temperature in a hydrogenation was 98 degrees C.

[0022] There is having collected the hydrogenation conditions of the above examples 1-4 and the examples 1-4 of a comparison and the result in Table 1.

[0023]

[Table 1]

表 1. 水添触媒条件と結果一覧

		実施例 1	実施例 2	実施例 3	実施例 4	比較例 1	比較例 2	比較例 3	比較例 4
水添触媒種		TPM/Li	TPM/Li	TC/TMAL	TC/TMAL	TPM/Li	TPM/Li	TC/TMAL	TC/TMAL
重合体 (ポリマー)		A	B	A	B	A	B	A	B
第一回	添加時水添率*	0%	0%	0%	0%	0%	0%	0%	0%
	水添触媒添加量	20 ppm	10 ppm	30 ppm	15 ppm	40 ppm	20 ppm	70 ppm	30 ppm
第二回	添加時水添率*	70%	61%	65%	75%	—	—	—	—
	水添触媒添加量	20 ppm	5 ppm	20 ppm	5 ppm	—	—	—	—
第三回	添加時水添率*	—	85%	80%	88%	—	—	—	—
	水添触媒添加量	—	5 ppm	10 ppm	5 ppm	—	—	—	—
第四回	添加時水添率*	—	—	90%	93%	—	—	—	—
	水添触媒添加量	—	—	10 ppm	5 ppm	—	—	—	—
水添反応所要時間		35分	45分	30分	35分	65分	105分	30分	70分
Total 触媒添加量		40 ppm	20 ppm	70 ppm	30 ppm	40 ppm	20 ppm	70 ppm	30 ppm
最終水添率**		99.9%	99.8%	100%	99.9%	96.8%	85.1%	91.0%	89.2%

*各触媒添加時における、水素ガス消費量から推定した、重合体中に含まれる共役ジエン単位の水添率

NMR法(*)で測定された、重合体中に含まれる共役ジエン単位の水添率

***重水素化クロロホルムを溶媒に用い、270MHz、¹H-NMR スペクトルを基に測定。

[0024]

[Effect of the Invention] In order that this invention may obtain the conjugated-diene system polymer of 98% or more of the rates of a hydrogenation industrially using three or more big 1m reaction containers, in case a hydrogenation is carried out using a metallocene system hydrogenation catalyst, it is dividing a hydrogenation catalyst into several order and adding, and offers the industrial very advantageous technique of carrying out a hydrogenation certainly stably in the few amount of hydrogenation catalysts for a short time.

[Translation done.]

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(54) 【発明の名称】 改良された共役ジエン系重合体の水添方法

(57) 【要約】

【課題】 工業的に1m³以上の大きな反応容器内で、チタノセン系触媒を用いて、水素と接触させて共役ジエン系重合体の二重結合を水素添加し、98%以上の高水添率の共役ジエン系重合体を得る際に、なるべく少ない触媒使用量で、短時間で安定に高水添を達成する、工業的に有利な方法を提供するものである。

【解決手段】 有機アルカリ金属化合物を重合開始剤として重合した共役ジエン系重合体をメタロセン系水素添加触媒を用いて水素添加し、水素添加率98%以上の共役ジエン系重合体を得る際、水素添加触媒を2回以上に分けて添加し水素添加を進める事の特徴とする改良された共役ジエン系重合体の水素添加方法。

【特許請求の範囲】

【請求項1】 有機アルカリ金属化合物を重合開始剤として重合した共役ジエン系重合体をメタロセン系水素添加触媒を用いて水素添加し、水素添加率98%以上の共役ジエン系重合体を得る際、水素添加触媒を2回以上に分けて添加し水素添加を進める事の特徴とする改良された共役ジエン系重合体の水素添加方法。

【請求項2】 請求項1において、共役ジエン系重合体の水素添加率が60%～95%の時点で、1回以上水素添加触媒を追添する事の特徴とする改良された共役ジエン系重合体の水素添加方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、有機アルカリ金属化合物を重合開始剤として重合した共役ジエン系重合体を、メタロセン系水素添加触媒を用いて、水素と接触させて共役ジエンの二重結合を水素添加する方法に関する。更には、その際、工業的に1m³以上の大きな反応容器を用いて、水素添加率98%以上の共役ジエン系重合体を得る際、水素添加触媒を数次に分けて添加する事により、安定に、また短時間で経済的に水素添加する方法に関する。

【0002】

【従来の技術】 メタロセン系触媒は、重合体の水素添加（以下水添と略す）に用いる場合、ニッケル系触媒に比べれば、よりマイルドな条件下で、より少ない量で同量の水添を成し遂げるという特徴が有り、この為、水添後、触媒残差を取り除く特別な処理が必要なく、又、たとえ行う場合も触媒残差を取り除く処理が軽くて済むという特徴が有るため、近年、よく使われるようになってきた。しかしメタロセン系触媒は、価格が高く、また容易に活性を失い易いという問題を有するため、従来、より高活性で、取扱い方が易しく長期貯蔵安定性の良い水添触媒が種々検討され提案されてきた。例えば、特定のチタノセン化合物とアルキルリチウムを組み合わせ、オレフィン化合物を水添する方法（特開昭61-33132号、特開平1-53851号）、メタロセン化合物と有機アルミニウム、亜鉛、マグネシウムと組み合わせでオレフィン性不飽和（共）重合体を水添する方法（特開昭61-28507号、62-209103号）、特定のチタノセン化合物とアルキルリチウムとの組合せでオレフィン性不飽和基含有リビングポリマーを水添させる方法（特開昭61-47706号、特開昭63-5402号）、チタノセン化合物とトリメチルアルミニウムのメタラサイクル化合物であるTebbe試薬とアルキルアルカリ金属化合物を組み合わせた反応物によるオレフィン性不飽和二重結合含有ポリマー中のオレフィン性二重結合を水添する方法（米国特許5244980号）、チタノセン化合物を、特定された量のリチウムアルコキシと組み合わせオレフィン性不飽和二重結合

含有ポリマー中のオレフィン性二重結合を水添する方法（特開平1-275605）、メタロセン系水添触媒を用い、特定比率で有機アルミニウム化合物その他を存在させた系で共役ジエン重合体を水添する方法（特願平9-252180）等の方法が提案されている。

【0003】

【本発明が解決しようとする課題】 しかしながら、この様ないずれの方法においても、実際に工業的に1m³以上の大きな反応容器内で、98%以上の高水添率の共役ジエン系重合体を得ようとする、温度変化などで水添条件が変動したり、触媒使用量を経済性追求のため減らしたりすると、水添時間が長くなったり、はなはだしくは目的の高水添率の重合体を得られないなどのトラブルが生じた。この為、なるべく少ない触媒使用量で、工業的に短時間で安定に高水添を達成する為の水添方法の改良が望まれていた。

【0004】

【課題を解決するための手段】 本発明者らは従来技術の上記の問題点を解決すべく鋭意検討した結果、このような1m³以上の大きな反応容器内で水添を行う場合、水添触媒を数次に分けて添加する事、好ましくは特に特定の水添率で必ず1回以上触媒を追添する事により、工業的に安定に短時間で経済的に、高水添率の水添を達成する方法を見つけ出し、本発明を成すに至った。

【0005】 本発明は、1m³以上、好ましくは5m³以上、さらに好ましくは10m³以上の大きな反応容器を用いて工業的に、有機アルカリ金属化合物を重合開始剤として重合した共役ジエン系重合体をメタロセン系水添触媒を用いて水添し、水添率98%以上の共役ジエン系重合体を得る際、水添触媒を2回以上、好ましくは2～10回に分けて添加し水添を進める事、更に好ましくは、重合体の水添率が60%～95%の時点で、1回以上水添触媒を追添する事の特徴とする改良された共役ジエン系重合体の水添方法である。

【0006】 本発明で重合開始剤として用いられる有機アルカリ金属化合物は、一般的に共役ジエン化合物に対しアニオン重合活性があることが知られている脂肪族炭化水素アルカリ金属化合物、芳香族炭化水素アルカリ金属化合物、有機アミノアルカリ金属化合物等が含まれ、アルカリ金属としてはリチウム、ナトリウム、カリウム等である。好適な有機アルカリ金属化合物としては、炭素数1から20の脂肪族および芳香族炭化水素リチウム化合物であり、1分子中に1個のリチウムを含む化合物、1分子中に複数のリチウムを含むジリチウム化合物、トリリチウム化合物、テトラリチウム化合物が含まれる。具体的にはn-プロピルリチウム、n-ブチルリチウム、sec-ブチルリチウム、tert-ブチルリチウム、n-ペンチルリチウム、n-ヘキシルリチウム、ベンジルリチウム、フェニルリチウム、トリルリチウム、ジイソプロピルベンゼンとsec-ブチルリチ

ウムの反応生成物、さらにジビニルベンゼンとsec-ブチルリチウムと少量の1, 3-ブタジエンの反応生成物等があげられる。

【0007】本発明の共役ジエン系重合体は、共役ジエンのホモ重合体、2種以上の共役ジエンからなる共役ジエンの共重合体、また共役ジエンと共重合可能な他の単量体との共重合体であって、該重合体中に共役ジエンから由来するオレフィン2重結合を有する1, 4-重合体、1, 2または3, 4-重合体を含むものである。共役ジエンとしては、炭素数4から20の炭素原子を有する共役ジエン、具体的には1, 3-ブタジエン、イソブレン、2, 3-ジメチル-1, 3-ブタジエン、1, 3-ペンタジエン、2-メチル-1, 3-ペンタジエン、1, 3-ヘキサジエン、4, 5-ジエチル-1, 3-オクタジエン、3-ブチル-1, 3-オクタジエン等が挙げられる。工業的に有利に展開でき、物性の優れた弾性体を得る上からは、1, 3-ブタジエン、イソブレンが好ましい。また、共役ジエンと共重合可能な他の単量体として代表的なものはビニル芳香族化合物である。例えばスチレン、 α -メチルスチレン、p-メチルスチレン、ジビニルベンゼン、1, 1-ジフェニルエチレン、N, N-ジメチル-p-アミノエチルスチレン、N, N-ジエチル-p-アミノエチルスチレン等があげられ、好ましくはスチレン、 α -メチルスチレンである。これらの共重合体はランダム、またはブロック共重合体である。

【0008】水添は通常不活性化水素溶媒中で行われるが、この不活性化水素溶媒としては、共役ジエン系重合体の溶媒であって水素添加の際に反応に悪影響を与えないものである。本発明ではさらに、重合に引き続いて同じ不活性化水素溶媒中で水素添加が行われることが好ましい。好適な溶媒は、例えばn-ブタン、イソブタン、n-ペンタン、n-ヘキサン、n-ヘプタン、n-オクタンの如き脂肪族炭化水素類、シクロヘキサン、シクロヘプタン、メチルシクロヘプタンの如き脂環式炭化水素類、また、ベンゼン、トルエン、キシレン、エチルベンゼンの如き芳香族炭化水素も、選択された水添条件下で芳香族二重結合が水添されない時に限って使用することができる。この溶媒中に溶かす共役ジエン系重合体の濃度は、5~40%、好ましくは10~30%の濃度にする。この濃度が5%より低いと、共役ジエン系重合体と溶媒を分離する後工程の負荷が大きくなり好ましくなく、40%を越える濃度であると粘度がはなはだしく高くなり、水素、水添触媒などとの混合性や伝熱性が低下し、ひいては水添反応に影響するため好ましくない。

【0009】本発明で用いられるメタロセン系水添触媒は、配位子として同一又は異なる2個の(置換)シクロペンタジエニル基を持つチタン、ジルコニウム、ハフニウム等の有機金属化合物であり、好ましくは還元性の有

機金属化合物、例えばアルキルリチウム、アルキルマグネシウム、アルキルアルミニウム、アルキル亜鉛等と用いられる。水添方法としては、メタロセン系化合物を用いる水添方法であればどの方法も採用できる。例えば、特定のチタノセン化合物とアルキルリチウムを組み合わせ、オレフィン化合物を水添する方法(特開昭61-33132号、特開平1-53851号)、メタロセン化合物と有機アルミニウム、亜鉛、マグネシウムと組み合わせでオレフィン性不飽和(共)重合物を水添する方法(特開昭61-28507号、62-209103号)、特定のチタノセン化合物とアルキルリチウムとの組合せでオレフィン性不飽和基含有リビングポリマーを水添させる方法(特開昭61-47706号、特開昭63-5402号)、チタノセン化合物とトリメチルアルミニウムのメタラサイクル化合物であるTebbe試薬とアルキルアルカリ金属化合物を組み合わせた反応物によるオレフィン性不飽和二重結合含有ポリマー中のオレフィン性二重結合を水添する方法(米国特許5244980号)、チタノセン化合物を、特定された量のリチウムアルコキシサイトと組み合わせオレフィン性不飽和二重結合含有ポリマー中のオレフィン性二重結合を水添する方法(特開平1-275605)、メタロセン系水添触媒を用い、特定比率で有機アルミニウム化合物その他を存在させた系で共役ジエン重合物を水添する方法(特願平9-252180)等の何れの方法でも良い。また水添条件も、この様な水添触媒に合わせた、各明細書に書かれた方法を用いる事ができる。

【0010】このような水添触媒を、当初の1回を含めて2回以上、好ましくは2~10回に分け、更に好ましくは2~5回に分けて添加する。この場合、最低2回に分け、好ましくは、重合体の水添率が60%~95%の時点で、更に好ましくは70%~95%の時点で、少なくとも1回以上水添触媒を追添する事がきわめて重要である。すなわちメタロセン系水添触媒を用いて1m³以上の工業的な反応容器内で水添を行うと、重合体ポリマー溶液の水添率が60%~95%と上昇すると粘度も大幅に上昇し、除熱能力が悪化し、局所的な温度上昇が発生し易くなる。特に水添反応は激しい発熱反応であり、この傾向は著しい。局所的な温度上昇が発生すると、その部分の水添反応はますます活性化し、更なる発熱を引き起こし、最後には水添触媒の活性が喪失する触媒の失活反応を引き起こす。このため、結果的に水添反応の低下や甚だしくは目的の高水添率の重合体が得られないなどのトラブルが起こり易い。この現象は大型の反応器ほど顕著であり、工業的な生産をおこなう際の大きな課題である。しかし、このような水添率に達した時点で触媒を追添する事で、必要な時点で必要な量の活性触媒を供給でき、多段に追添することで、全触媒使用量としてはむしろ少なくとも、短時間で確実に安定に98%以上という高水添率の重合体を得るまで水添する事が可能とな

る。水添触媒は、最初の1回目の添加分は重合体と触れた後で活性化しても良いが、少なくとも追添触媒は、水添活性を発現した後か水素雰囲気ですぐに活性化する状態で添加する事が好ましい。数次添加の水添触媒は、初回添加分と後添加の触媒は同じ物でなくてもかまわないが、同じ物の方が、運転の簡便性から望ましい。更に11回以上に分けて添加する事は、操作が煩雑になり好ましくなく、2~10回、望ましくは2~5回、更に望ましくは2~3回に分けていれる事は、操作性と触媒効率や水添確実性を両立でき好ましい。触媒追添時期である、重合体の水添率が60%~95%の時点、更に好ましくは70%~95%の時点とを判別する方法としては、水添された共役ジエン系重合体の二重結合の残存量の測定、使用された水素ガス量からの算出、水添容器内の水素圧力変化、水添時間など何れの指標を基に判別しても良い。更に重合体の水添率が60%~95%の時点、更に好ましくは70%~95%の時点まで、特定の容器内でバッチ式又は連続及び又は回分式に水添を行い、水添触媒を追添し別の容器や配管内で98%まで残りの部分の水添を行ってもよい。いずれにしても、このように分割して水添触媒を添加する事により効率的でしかも安定で確実に工業的に水添を行う事ができる。なお本発明における水添率は、重合体中に含まれる共役ジエン単位の水添率を意味する。

【0011】

【実施例】以下の実施例により本発明を具体的に説明するが、本発明はこれらに限定されるものではない。実施例に用いた各リビングポリマー（Aポリマー及びBポリマー）の合成例を以下の製造例に示した。

【0012】製造例1

16m³の攪拌機付き反応器中にシクロヘキサン4.3トン、スチレンモノマー0.20トンを入れた後、15%n-ブチルリチウム溶液4.8kg、更にテトラメチルエチレンジアミン0.62kgを加え、初期温度を70℃に設定し攪拌下で40分間重合した。次いで、1,3-ブタジエンモノマーを30%含むシクロヘキサン溶液を3.08トン追加し1時間重合した。更にスチレンモノマーを30%含むシクロヘキサン溶液を0.66トン追加し40分間重合した。重合時のピーク温度は82℃であった。得られたリビングポリマー（Aポリマー）は、結合スチレン含有量30%、ブロックスチレン含有量30%、ブタジエン単位の1,2-ビニル結合含有量37%であり、数平均分子量が約23万であるスチレン-ブタジエン-スチレン型リビングブロックポリマーであった。

【0013】製造例2

16m³の攪拌機付き反応器中にシクロヘキサン4.85トン、スチレンモノマー0.33トンを入れた後、15%n-ブチルリチウム溶液22kgを加え、更にテトラメチルエチレンジアミン1.7kgを加え、初期温度

を70℃に設定し攪拌下で30分間重合した。次いで、1,3-ブタジエンモノマーを30%含むシクロヘキサン溶液を5.18トン追加し45分間重合した。更にスチレンモノマーを30%含むシクロヘキサン溶液を1.11トン追加し30分間重合した。重合時のピーク温度は、85℃であった。得られたリビングポリマー（Bポリマー）は、結合スチレン含有量30%、ブロックスチレン含有量30%、ブタジエン単位の1,2-ビニル結合含有量39%である数平均分子量が約6.1万のスチレン-ブタジエン-スチレン型リビングブロックポリマーであった。

【0014】実施例1

特開平8-33846の方法に準拠した方法により水添触媒調製を行った。すなわち、ビス（シクロペンタジエニル）チタニウムジ-*p*-トリル（TPM）6kgをシクロヘキサン526kg中に溶解し、液状1,2-ポリブタジエン60kgを添加した後、15%ブチルリチウム溶液を7.1kg添加、更にはエタノール0.6kgを添加し反応させ、水添触媒（TPM/Li）として調製した。一方、水添の前処理として、製造例1で得られたリビングポリマー（Aポリマー）溶液に、精製乾燥したシクロヘキサンを加えて11%のポリマー濃度のシクロヘキサン溶液に調整し、更に重合触媒であるn-ブチルリチウムの0.8等量モル分エチルアルコールを加えた。このポリマー溶液を20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。ここに、先ほど調製した水添触媒（TPM/Li）を、Ti重量基準でポリマー重量に対し20ppm添加し水添を開始した。23分後、水素ガスの消費量からみたポリマーの水添率が70%となり、この時点で、更に、水添触媒（TPM/Li）をTi重量基準で20ppm追加し、水添を継続した。35分後、水素ガスの消費量からみたポリマーの水添率が100%となり、水素のポリマー溶液への吸収も停止したので水添を終了し、NMR法によりポリマーの水添率を測定したところ99.9%であった。なお水添中の最高到達温度は95℃であった。

【0015】比較例1

製造例1と同様の方法で得られたリビングポリマー（Aポリマー）溶液を、実施例1と同様の方法で前処理した後、20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、0.7MPaの水素ガス加圧下とした。これに、Ti重量基準でポリマー重量に対し40ppmとなるように実施例1と同様の方法で調製した水添触媒（TPM/Li）を添加し、水添を開始した。65分後、水素ガスの消費量からみたポリマーの水添率は97%であったが、水素のポリマー溶液への吸収がほぼ停止していたため、水添を終了した。NMR法による最

終ポリマーの水添率は96.8%であった。なお水添中の最高到達温度は100℃であった。

【0016】実施例2

前処理として、製造例2で得られたリビングポリマー

(Bポリマー)に、精製乾燥したシクロヘキサンを加えて19%のポリマー濃度のシクロヘキサン溶液に調整した後、エチルアルコールをn-ブチルリチウムの0.9等量モル分加えた。次いでこのポリマー溶液を20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。Ti重量基準でポリマー重量に対し10ppmとなるように、実施例1と同様の方法で調製された水添触媒(TPM/Li)を反応容器内に添加し、水添を開始した。35分後、水素ガスの消費量からみたポリマーの水添率が61%となり、この時点で、Ti重量基準で5ppmとなる量の水添触媒(TPM/Li)を追加し、水添を継続した。40分後、水素ガスの消費量からみたポリマーの水添率が85%の時点で更にTi重量基準で5ppm追加し、水添を継続した。45分後、水素ガスの消費量からみたポリマーの水添率が100%となり、水素のポリマー溶液への吸収も停止したので水添を終了し、NMR法によりポリマーの水添率を測定したところ99.8%であった。なお水添中の最高到達温度は90℃であった。

【0017】比較例2

製造例2と同様の方法で得られたリビングポリマー(Bポリマー)溶液を、実施例2と同様の方法で前処理した後、20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。更に、実施例1と同様の方法で調製された水添触媒(TPM/Li)をTi重量基準でポリマー重量に対し20ppm添加し、水添を開始した。105分後、水素ガスの消費量からみたポリマーの水添率は85%で有ったが、水素のポリマー溶液への吸収がほぼ停止していたため、水添を終了し、NMR法による最終ポリマーの水添率を測定したところ、水添率は85.1%であった。なお水添中の最高到達温度は95℃であった。

【0018】実施例3

特願平9-252180の方法に準拠した方法により水添触媒調製を行った。ビス(シクロペンタジエニル)チタニウムジクロライド5kgをシクロヘキサン70.1kgに添加し、攪拌後、10%トリメチルアルミニウム溶液24.9kgを追加し72時間反応させ、水添触媒(TC/TMAL)溶液として調製した。一方、製造例1で得られたと同様のリビングポリマー(Aポリマー)溶液を、実施例1と同様の方法で前処理した後、20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガス

で置換し、更に0.7MPaの水素ガス加圧下とした。ここに、先ほど調製した水添触媒(TC/TMAL)をTi重量基準で、ポリマー重量に対し30ppm添加し水添を開始した。20分後、水素ガスの消費量からみたポリマーの水添率が65%となり、この時点で、水添触媒(TC/TMAL)をTi重量基準で更に20ppm追加し、水添を継続した。23分後、水素ガスの消費量からみたポリマーの水添率が80%となった時点で、水添触媒(TC/TMAL)をTi重量基準で更に10ppm追加し、水添を継続した。更に、水添開始から27分後、水素ガスの消費量からみたポリマーの水添率が90%となった時点で、水添触媒(TC/TMAL)をTi重量基準で更に10ppm追加し、水添を継続した。30分後、水素ガスの消費量からみたポリマーの水添率が100%となり、水素のポリマー溶液への吸収も停止したので水添を終了し、NMR法によりポリマーの水添率を測定したところ100%であった。なお水添中の最高到達温度は98℃であった。

【0019】比較例3

製造例1と同様の方法で得られたリビングポリマー(Aポリマー)溶液を、実施例1と同様の方法で前処理した後、20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。更に実施例3と同様の方法で調製された水添触媒(TC/TMAL)をTi重量基準で、ポリマー重量に対し70ppm添加し水添を開始した。30分後の水素ガスの消費量からみたポリマーの水添率は91%で有り、水素のポリマー溶液への吸収もほぼ停止しており、NMR法によるポリマーの水添率は91.0%であった。なお水添中の最高到達温度は102℃であった。

【0020】実施例4

製造例2と同様の方法で得られたリビングポリマー(Bポリマー)溶液を、実施例2と同様の方法で前処理した後、20m³の攪拌機付き反応器に全量移送した。攪拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。更に実施例3と同様の方法で調製された水添触媒(TC/TMAL)をTi重量基準で、ポリマー重量に対し15ppm添加し水添を開始した。25分後、水素ガスの消費量からみたポリマーの水添率が75%となり、この時点で、水添触媒(TC/TMAL)をTi重量基準で更に5ppm追加し、水添を継続した。29分後、水素ガスの消費量からみたポリマーの水添率が88%の時点で水添触媒(TC/TMAL)をTi重量基準で更に5ppm追加し、水添を継続した。更に水添開始から32分後、水素ガスの消費量からみたポリマーの水添率が93%の時点で水添触媒(TC/TMAL)をTi重量基準で更に5ppm追加し、水添を継続した。35分後、水素ガスの消費量からみたポリマーの水添率

が100%となり、水素のポリマー溶液への吸収も停止したので水添を終了し、NMR法によりポリマーの水添率を測定したところ99.9%であった。なお水添中の最高到達温度は89℃であった。

【0021】比較例4

製造例2と同様の方法で得られたリビングポリマー（Bポリマー）溶液を、実施例2と同様の方法で前処理した後、20m³の撹拌機付き反応器に全量移送した。撹拌下で反応器内を初期温度80℃に設定した後、反応器内を水素ガスで置換し、更に0.7MPaの水素ガス加圧下とした。更に実施例3と同様の方法で調製された水添

表1. 水素添加条件と結果一覧

	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2	比較例3	比較例4
水添触媒種	TPM/Li	TPM/Li	TC/TMAL	TC/TMAL	TPM/Li	TPM/Li	TC/TMAL	TC/TMAL
重合体（ポリマー）	A	B	A	B	A	B	A	B
第一回	添加時水添率*	0%	0%	0%	0%	0%	0%	0%
	水添触媒添加量	20 ppm	10 ppm	30 ppm	15 ppm	40 ppm	20 ppm	70 ppm
第二回	添加時水添率*	70%	61%	65%	75%	—	—	—
	水添触媒添加量	20 ppm	5 ppm	20 ppm	5 ppm	—	—	—
第三回	添加時水添率*	—	85%	80%	88%	—	—	—
	水添触媒添加量	—	5 ppm	10 ppm	5 ppm	—	—	—
第四回	添加時水添率*	—	—	90%	93%	—	—	—
	水添触媒添加量	—	—	10 ppm	5 ppm	—	—	—
水添反応所要時間		35分	45分	30分	35分	65分	105分	30分
Total 触媒添加量		40 ppm	20 ppm	70 ppm	30 ppm	40 ppm	20 ppm	70 ppm
最終水添率**		99.9%	99.8%	100%	99.9%	96.8%	85.1%	91.0%

*各触媒添加時における、水素ガス消費量から推定した、重合体中に含まれる共役ジエン単位の水添率

NMR法(*で測定された、重合体中に含まれる共役ジエン単位の水添率

***重水素化クロロホルムを溶媒に用い、270MHz、¹H-NMR スペクトルを基に測定。

【0024】

【発明の効果】本発明は、1m³以上の大きな反応容器を用いて工業的に、水添率98%以上の共役ジエン系重合体を得る為、メタロセン系水添触媒を用いて水添する

触媒（TC/TMAL）をTi重量基準で、ポリマー重量に対し30ppm添加し水添を開始した。70分後、水素ガスの消費量からみたポリマーの水添率は89%で有り、水素のポリマー溶液への吸収もほぼ停止した。この時点でのNMR法によるポリマーの水添率は89.2%であった。なお水添中の最高到達温度は98℃であった。

【0022】以上の実施例1～4、比較例1～4の水添条件と結果を纏めたのが、表1で有る。

【0023】

【表1】

際、水添触媒を数次に分けて添加する事で、少ない水添触媒量で安定に短時間で確実に水添できる工業的に極めて有利な方法を提供するものである。

フロントページの続き

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